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Hybrid High-Temperature Nanostructured Magnets

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ABSTRACT

The hysteretic behavior of two-phase permanent magnets for high-temperature applications is examined. A variety of systems have been synthesized and investigated, including Sm-Co-Cu-Ti bulk magnets, $SmCo_5$:Cu-Ti thin-film materials, and mechanically milled Sm-Co-Zr magnets. The hybrid character of the material leads to very high room-temperature coercivities, between 30.2 and 43.6 kOe, and to the survival of a comparatively large part of the coercivity at high temperatures (12.3 kOe at 500 °C for $SmCo_{6.5}Cu_{0.8}Ti_{0.3}$). The coercivity reflects the structure and chemical composition of the material. When ferromagnetic grains are separated by a ferromagnetic boundary phase, the boundary phase acts as a pinning center, but when the grain-boundary phase has a comparatively low Curie temperature, the high-temperature magnetism of the system is that of a weakly interacting ensemble of magnetic particles. In spite of some residual paramagnetic exchange coupling, which is discussed in this work, this mechanism enhances the coercivity.

INTRODUCTION

Recently there has been a resurgence of interest in Sm-Co-based permanent-magnet alloys. The reasons for this are twofold. First, Sm_2Co_{17} and phases based on this composition have the highest known Curie temperature (T_c) and thus have the best chance of creating a practical magnet for use at high temperatures such as 500 °C. Second, $SmCo_5$ has the highest-known uniaxial anisotropy constant which leads generally to maximum values of coercivity. $SmCo_5$ also is a relatively high-temperature magnet. In the quest for new nanocomposite magnets based on the exchange coupling of hard and soft phases with nanoscale dimensions, the use of $SmCo_5$ as the hard phase has the major benefits of being both extremely hard and a high-temperature magnet. The clear challenge for workers in the design of high-temperature and high-energy product nanoscale magnets is to synthesize hybrid systems that exploit the properties of at least two phases to create magnets with much improved figures of merit including operating temperature and coercivity.

In this paper we present results of recent work in our laboratories based on controlling the nanostructure and phase mixtures of hybrid or composite magnets based on $SmCo_5$ (1:5), Sm_2Co_{17} (2:17), $SmCo_7$ (1:7) and related compounds. First, we discuss a series of Sm-Co-Cu-Ti alloys containing 2:17 and 1:5 phases. This system has a cellular structure and has produced the highest known coercivity (H_c) at 500 °C (12.3 kOe). Second, we outline results on $SmCo_5$:Cu-Ti nanocomposite magnets prepared in thin-film form with sputtering methods. These magnets have led to H_c values above 40 kOe at 295 K. Third, the technique of mechanical milling has been used to prepare two-phase magnets containing $SmCo_5$. These systems also have large H_c

values (> 30 kOe) at room temperature. Finally, in an outlook section, we discuss the magnetic behavior of conceivable two-phase magnets where the grain-boundary phase is paramagnetic.

Sm-Co-Cu-Ti HYBRID BULK MAGNETS

Renewed impetus for better high-temperature magnet materials has come from demands for aircraft engine components functioning at temperatures to about 500 °C. Conventional $Sm_2(Co,Fe,Cu,Zr)_{17}$ permanent magnets have large energy products and coercivities at room temperature. In the last couple of years efforts have been made to improve the properties of this class of material by adjusting the composition and H_c values up to 10 kOe have been obtained at 500 °C [1]. Recently we have discovered a relatively simple Sm-Co-Cu-Ti alloy that consists of two phases, 2:17 and 1:5, and which has a positive dH_c/dT and H_c values above 10 kOe at 500 °C [2,3]. We discuss here our most recent improvements in this material and our understanding of its behavior.

Alloys of the form $SmCo_{7.05-x-y}Cu_xTi_y$, where $0.4 \leq x \leq 0.9$ and $y = 0.25$ or 0.3, were prepared by arc melting under flowing argon. The samples generally were heat treated by annealing in argon at 1165 °C for 3 hrs., cooled to 825 °C and annealed for 8 hrs., followed by slow cooling to 550 °C at the rate of 1 °C/min. Characterization methods include x-ray diffraction (XRD), transmission electron microscopy (TEM), and magnetization with SQUID or VSM to 600 °C. XRD results show that the arc melted samples had the disordered 1:5 structure (the so-called 1:7 structure). After the heat treatment the structure reverts into two phases: 2:17 and 1:5. This is shown clearly by the thermomagnetic data of Figure 1, where the T_c values of Sm_2Co_{17} (~920 °C) and a doped $SmCo_5$ phase (~700 °C) are seen. TEM micrographs show a cellular nanostructure reminiscent of the conventional 2:17 magnets. The 2:17 cells have dimensions of order 70 nm and the 1:5 boundary phase has a thickness of order 10 nm.

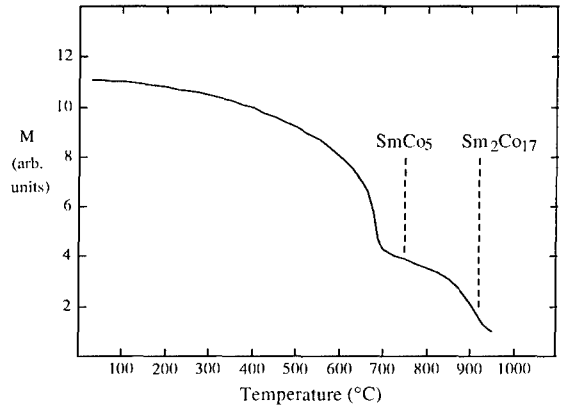


Figure 1. Thermomagnetic analysis of $SmCo_{6.1}Cu_{0.6}Ti_{0.3}$ magnet. The dashed lines show the Curie temperatures of the pure Sm_2Co_{17} and $SmCo_5$ phases.

Figures 2 and 3 show examples of hysteresis loops at room temperature and elevated temperatures, respectively. The dependence of H_c on Cu content at 500°C and on temperature for three Cu concentrations is shown in Figures 4 and 5, respectively. Notable features of the data include a pinning controlled initial magnetization behavior and a high H_c value at 295K (Figure 2), and a positive contribution of Cu to the coercivity (Figure 4). To our knowledge, the H_c values of 13.8 kOe at 450 °C and 12.3 kOe at 500 °C are the largest ones reported at these temperatures. The sensitivity of the temperature dependence of H_c on Cu content is seen in Figure 5.

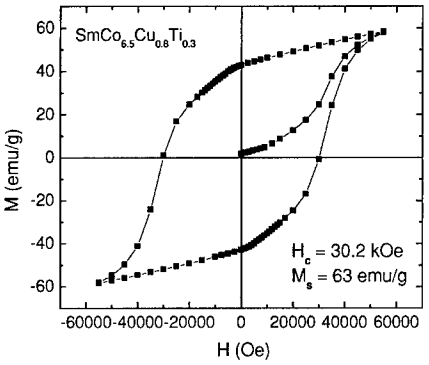


Figure 2. Hysteresis loop of $SmCo_{6.5}Cu_{0.8}Ti_{0.3}$ sample at room temperature.

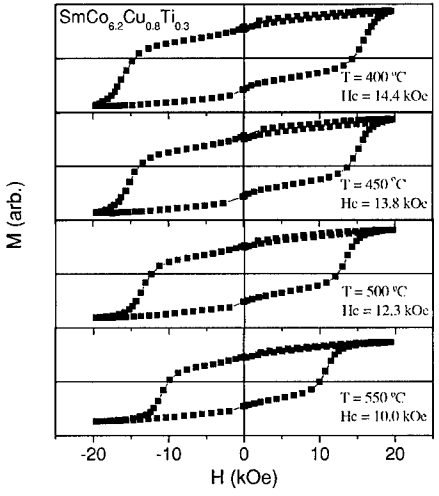


Figure 3. Hysteresis loops of $SmCo_{6.2}Cu_{0.8}Ti_{0.3}$ magnet at various temperatures.

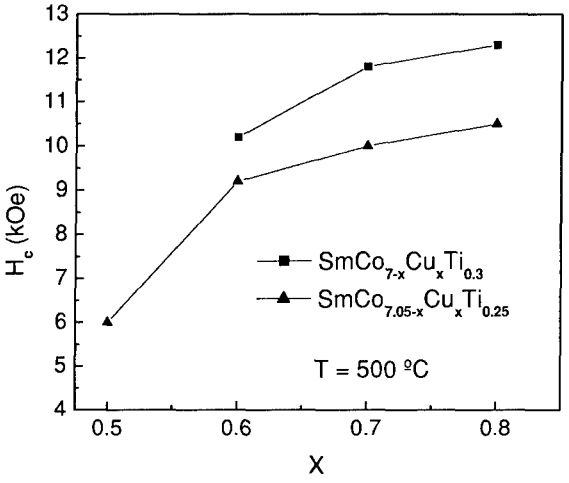


Figure 4. Influence of Cu concentrations on coercivity at 500 °C.

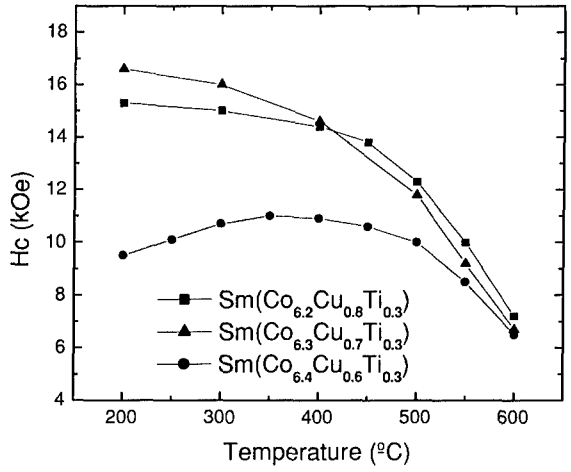


Figure 5. Temperature dependence of coercivity of $SmCo_{7-x}Cu_xTi_{0.3}$.

The temperature coefficient of the coercivity (TCC) can be explained in the following way. These magnets are of the pinning type in which the interaction of the domain wall with the grain boundary controls the behavior [4,5]. A detailed calculation gives

$$H_c = H_0\left(\frac{\pi}{3\sqrt{3}}\cdot\frac{b}{\delta}\cdot\frac{|\Delta K|}{K_h}\right) \quad (1)$$

where H_0 is the anisotropy field of the main (2:17) phase, K_h is the anisotropy constant of same phase, b is the thickness of the boundary (1:5) phase, δ is the domain-wall thickness, and $\Delta K = K_h - K_s$ where K_s is the anisotropy of the softer boundary phase [3]. By considering the expected temperature dependence of K_h and K_s and the expected dependence of K_s on Cu content, it is possible to rationalize the temperature dependence of $H_c(T)$ shown in Figure 5, including the maximum in $H_c(T)$ seen for the sample with x = 0.6.

A more thorough understanding of the magnetic behavior of these alloys, which we are now pursuing, will require quantitative estimates of the anisotropy of the boundary phase, $SmCo_{5-x}Cu_x$. In addition, these magnets do not contain Zr as do the conventional 2:17 magnets. Preliminary TEM results have not detected a Ti lamellar phase analogous to the Zr one in the conventional magnets. Thus further work is expected to lead to a better understanding of the nanostructure-properties relationship in these materials and, ideally, to further improvements in high-temperature properties.

$SmCo_5$:Cu-Ti NANOCOMPOSITE MAGNETS

We have seen in the above paragraphs that Sm-Co-based compounds, when suitably nanostructured, can produce interesting hard magnetic properties. In addition, earlier work in our laboratories has shown that multilayer sputtering can lead to hard:soft nanocomposite films with near record energy products at room temperature. Specifically, multilayered Fe/Pt films after annealing have been shown to produce FePt:$Fe_{1-x}Pt_x$ nanocomposites with the hard phase being $L1_0$-structure FePt and a soft Fe-rich $Fe_{1-x}Pt_x$ alloy interspersed in 5-10 nm grains in larger FePt grains [6]. The composite was shown to have an energy product, $(BH)_{max}$, of about 53 MGOe, close to the record of about 55 MGOe for $Nd_2Fe_{14}B$.

In the present studies we have made multilayers of the form

$$Si/Cr(90nm)/[SmCo_5/X]_n/Cr(18nm). \quad (2)$$

where Si is a single-crystal (001) silicon substrate. Cr is used as an underlayer and coating layer for protection against oxidation during annealing, typically in the range 475-550 °C. The magnetic layer consists of 200 nm of $SmCo_5$, $SmCo_5$/Cu, $SmCo_5$/Ti or $SmCo_5$/CuTi. n is the number of layers ranging from n = 1 (single layer) to n = 42. The sputtering techniques and annealing procedures have been described in earlier papers [7].

Preliminary results obtained on these systems include the following. $SmCo_5$ single layer and $SmCo_5$/Cu multilayers do not show any significant coercivity (H_c < 0.1 kOe) before and after annealing. $SmCo_5$/Ti multilayers exhibit H_c values of less than 10 kOe after annealing.

Figure 6 shows an XRD scan of a film with the initial structure Cr 90 nm/[($SmCo_5$) 4.5nm/ (Cu-Ti) 0.3 nm]$_{42}$/Cr 18 nm. The data are consistent with a nanostructure consisting of 1:5 grains with mostly random orientations. These films show large H_c values after annealing. Hysteresis loops at room temperature for $SmCo_5(Cu_{0.9}Ti_{0.1})_{0.6}$ are shown in Figure 7 which shows the effect of annealing temperature. There is a slight inflection point near H = 0, suggesting a second magnetic phase that is more strongly exchange coupled to the main hard phase for the higher annealing temperature (525 °C).

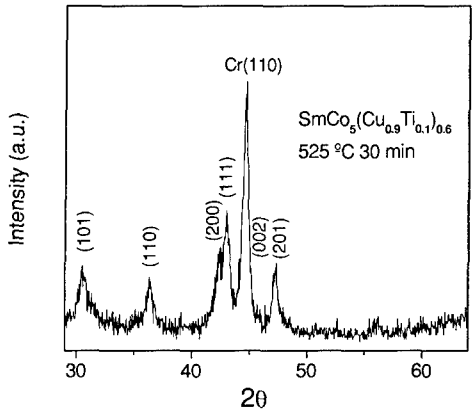


Figure 6. X-ray diffraction for thin films with the initial structure Cr 90 nm [($SmCo_5$)4.5 nm/ (CuTi)0.3 nm] x 42/Cr 18 nm.

The coercivity is large (43.6 kOe) and decreasing the Cu-Ti fraction by a factor of 2/3 leads to H_c = 41.0 kOe and slightly more evidence for an exchange decoupled second phase.

Electron microscopy studies clearly are needed to determine the nanostructure of these films, and are underway. If these films contain a weakly magnetic intergranular phase that pins domain walls, it may be possible through study of such systems to understand and create bulk magnets with similar structures and enhanced room- and high-temperature properties.

Sm-Co-Zr MECHANICALLY MILLED MAGNETS

The technique of mechanical milling and/or alloying is a well known method to create the nanostructure required for magnetic hardening [8-13]. Often, this approach amounts to creating such small grains (~ 10-20 nm) that the magnet to zero order can be regarded as an ensemble of uniaxial nanoparticles that approach a single random-anisotropy magnet with more or less exchange coupling between the nanograins [10,11]. If the composition of the original alloy, plus the nature of the heat treatment, permits or requires that there be more than a single phase present, then there is the possibility for either exchange decoupling or pinning of "interaction domain walls" by nonmagnetic or weakly magnetic intergranular phases. Alternatively, if the interface coupling between the granular and intergranular phases is favorable, there can be a

magnetization and energy-product enhancement, of course with a concomitant decrease in coercivity [11].

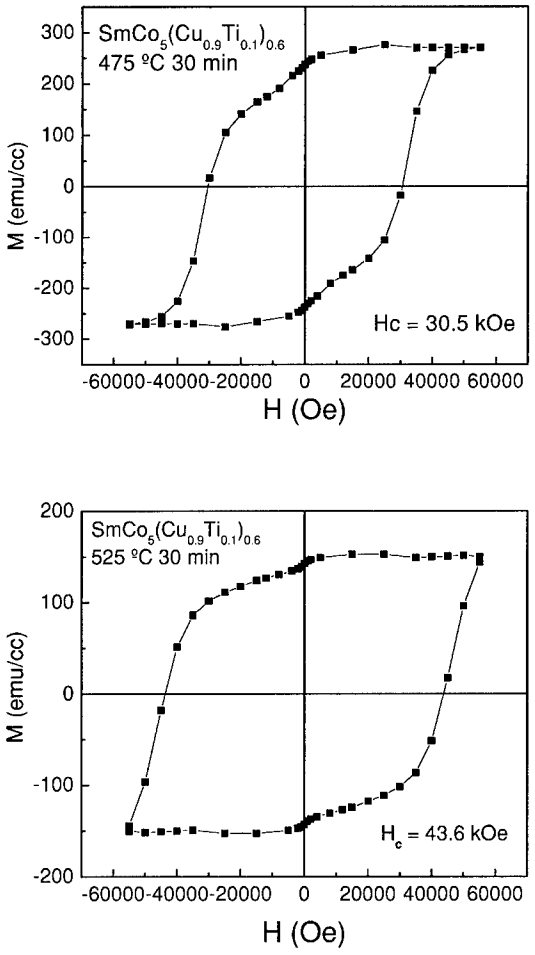


Figure 7. Hysteresis loops of $SmCo_5Cu$-Ti films with different annealing temperatures. The field is in the film plane.

The experiments to be described below involved mechanical milling of $Sm(Co,Zr)_{5.5}$ alloys. The idea was to examine the prospects for producing a hybrid magnet containing 1:5 and other Co-based phases with different anisotropies.

Nanostructured $Sm_{15.4}Co_{84.6-x}Zr_x$ (x = 0-5) magnet powders were synthesized by mechanical milling the as-cast alloys and appropriate annealing. The synthesis and handling of powders were performed under the protection of argon gas with high purity. The powders were milled for 10 hr, and annealed under high-purity argon gas atmosphere at temperature of 700 °C for 20 min. The phase configuration and structure were characterized for the as-cast alloys, milled powders and annealed powders with x-ray diffraction (XRD) with Cu K_α radiation.

Figure 8 shows the hysteresis loops measured at room temperature for the $Sm_{15.4}Co_{84.6-x}Zr_x$ (x = 0, 4) powders subjected to milling for 10 hr and annealing at 700 °C for 20 min. It is clear that high coercivity values can be obtained in these alloys. Comparing the two loops, the case with x = 0 shows a demagnetization behavior with less squareness while the x = 4 case indicates larger coercivity and good squareness. However, the remanent magnetization (M_r) is decreased in the powders with x = 4. Coercivity values up to 32 kOe were obtained in the powders with x = 4.

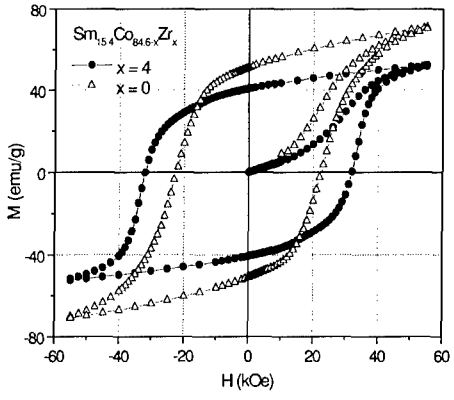


Figure 8. Magnetic hysteresis loops (at 295 K) for $Sm_{15.4}Co_{84.6-x}Zr_x$ (x = 0, 4) magnet powders.

Hard magnetic materials parameters (H_c and M_r) derived from the corresponding magnetic hysteresis loops are presented in Figure 9 for the $Sm_{15.4}Co_{84.6-x}Zr_x$ (x = 0-5) magnet powders. The coercivity value for the $Sm_{15.4}Co_{84.6-x}Zr_x$ (x = 0-5) magnet powders increases from 22.4 kOe for powders with x = 0 to about 32 kOe for powders with x = 4. However, the remanent magnetization decreases from about 51 emu/g for x = 0 to 37.6 emu/g for x = 5, that is, with increasing Zr content.

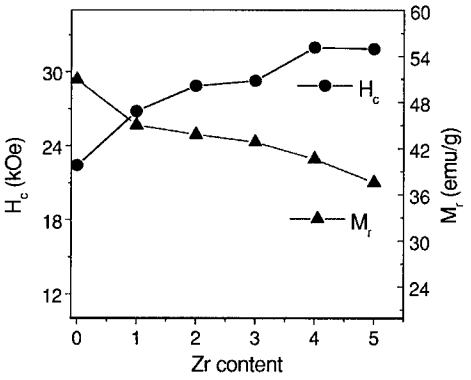


Figure 9. Dependence of room-temperature values of H_c and M_r upon Zr content in $Sm_{15.4}Co_{84.6-x}Zr_x$ (x = 0-5) magnet powders subjected to milling for 10 hr and annealing at 700 °C for 20 min.

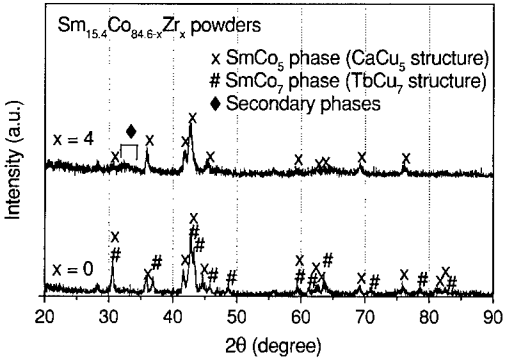


Figure 10. XRD patterns for $Sm_{15.4}Co_{84.6-x}Zr_x$ (x = 0 and 4) alloys powders subjected to milling for 10 hr and annealing at 700 °C for 20 min.

Figure 10 shows XRD data for x = 0 and 4 samples. For the undoped alloys the structure consists mainly of 1:5 and disordered 1:5 (that is, 1:7) grains. Upon alloying with Zr (x = 4), the lines can be indexed mostly with 1:5 structure lines, with evidence for a small admixture of secondary phases that are seen around 32-34 degrees. Sm-Co phases with x-ray lines in this region include Sm_2Co_7, and $SmCo_3$ which also have lines that overlap those of the 1:5 phase.

The grain size of the hard $SmCo_5$ phase evaluated by the Sherrer formula is about 16 nm for the x = 4 powders.

The magnetic hardening seen in Figure 8 as Zr is added to Sm-Co is difficult to understand without further understanding of the nanostructure, especially through TEM studies. The small sizes of the 1:5 grains and the presence of a small amount of secondary phases is consistent with a picture of pinning of interaction domain walls [11,14] as mentioned above. The magnetic characterization of the intergranular phase is needed to assess the possibilities for exchange coupling between the grains as well as the details of the magnetization reversal mechanism. Such characterization studies are underway.

HIGH-TEMPERATURE PERMANENT MAGNETS WITH PARAMAGNETIC BOUNDARY PHASES

One effect of additives such as Cu is to reduce the comparatively large Curie temperature of the cobalt-rich rare-earth intermetallics. In 2:17-1:5 Sm-Co hybrids, the Cu prefers to go into the grain-boundary phase, where it yields a pronounced reduction of the Curie temperature. Indirectly, this is exploited in commercial Sm-Co magnets and in some of the materials discussed in the previous sections: the Curie-temperature reduction in the grain-boundary phase leads to a reduced grain-boundary anisotropy, which enhances ΔK and improves, according to Eq. (1), the coercivity.

It is, however, conceivable to access the region where the grain-boundary phase is paramagnetic. This completely eliminates the harmful effect of domain walls jumping from one grain to the next grain and establishes a kind of Stoner-Wohlfarth behavior. Figure 11 illustrates the idea. Figure 11(a) shows the trapping of a domain wall between two ferromagnetic grains, whereas in Fig. 11(b) the grains are magnetically isolated. As shown in [15], two-phase magnets consisting of phases having different Curie temperatures exhibit a single well-defined and quite high Curie temperature, but at temperatures between the Curie temperatures of the phases the coupling between the 'ferromagnetic' regions is quite small when the thickness of the 'paramagnetic' grain-boundary phase is larger than a very few interatomic distances. This is the case for Sm-Co hybrid magnets, where the grain-boundary thickness is of the order of 5 nm, and where the Curie temperature of the Cu-rich grain boundary phase is significantly lower than the Curie temperature of the main phase.

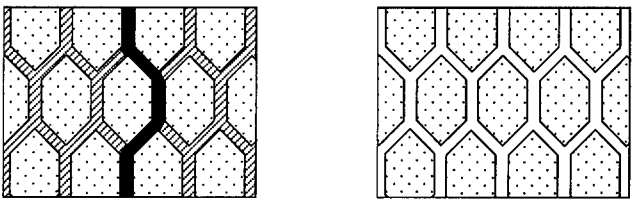
As a consequence, the magnets can be treated as a weakly interacting array of small particles. The corresponding exchange field between neighboring grains is

$$H_{ex} = c\, k_B T_c \frac{\exp(-t_B/\lambda)}{a^2 M_s R} \qquad (3)$$

Here λ is a decay length of the order of 0.3 nm, t_B is the thickness of the boundary region, R is the grain size, a is the lattice constant, T_c is the Curie temperature of the main phase, and c is a geometry and lattice-structure dependent constant of the order of one.

The magnetization reversal in these magnets is of the nucleation type [16]. In conventional Sm-Co hybrids, the regime described by Eq. (3) is realized above the Curie temperature of the grain boundary phase, which is quite high (about 650 °C in Fig. 1). However, by specific substitutions, such as adding very large amounts of Cu or other elements, it may be possible to yield a further suppression of the Curie temperature. This would cost a little bit of magnetization

but have a very positive effect on the coercivity, which is the most critical issue in high-temperature permanent magnetism.



(a) (b)

Figure 11. Magnetic structure of a cellular hybrid (a) below and (b) above the Curie temperature of the boundary phase. Magnetization reversal due to domain-wall motion is possible at low temperatures only.

CONCLUSIONS

We have discussed results of several methods for producing hard magnetic nanostructures containing two or more magnetic phases. Clearly there is a need for detailed nanostructure information to understand the secondary phases and their effect on the magnetization reversal mechanism. Theoretical mechanisms involving pinning and paramagnetic grain boundary phases have been discussed and applied to certain of the nanostructured magnets studied experimentally. Further research combining experimental and theoretical work on hybrid magnets of the type discussed here may well lead to new hard magnets with excellent high-temperature properties.

ACKNOWLEDGMENTS

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[16] Localized nucleation rather than coherent rotation or curling; the critical single-domain size is irrelevant in this context (see e.g. R. Skomski and J. M. D. Coey, "Permanent Magnetism", Institute of Physics, Bristol and Philadelphia 1999).